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HAWAII AGRICULTURAL EXPERIMENT STATION,
E. V. WILCOX, Special Agent in Charge.

Bulletin No. 30.

THE EFFECT OF HEAT ON HAWAIIAN SOILS.

BY

W. P. KELLEY,
Chemist,

AND

WILLIAM McGEORGE,
Assistant Chemist.

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HAWAII AGRICULTURAL EXPERIMENT STATION, HONOLULU.

[Under the supervision of A. C. TRUE, Director of the Office of Experiment Stations, United States Department of Agriculture.]

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LETTER OF TRANSMITTAL.

HONOLULU, HAWAII, *August 15, 1913.*

SIR: I have the honor to submit herewith and recommend for publication, as Bulletin 30 of the Hawaii Agricultural Experiment Station, a paper dealing with the Effect of Heat on Hawaiian Soils, by W. P. Kelley, chemist, and William McGeorge, assistant chemist of the station. The effect of heat upon Hawaiian soils, including highly manganiferous soils, has been found to be decidedly beneficial to the growth of all kinds of plants. The careful study of the various chemical and mechanical changes produced in soils by the application of heat, as set forth in this bulletin, throws considerable light upon the reasons for this beneficial effect. Studies on the effects of heat on soils have usually been confined to a few plant-food elements, whereas in this bulletin a large number of the inorganic and organic substances are considered. The bulletin is, therefore, considered a distinct contribution to the literature of this interesting phase of soil work.

Respectfully,

E. V. WILCOX,
Special Agent in Charge.

Dr. A. C. TRUE,
Director Office of Experiment Stations,
U. S. Department of Agriculture, Washington, D. C.

Publication recommended.
A. C. TRUE, *Director.*

Publication authorized.
D. F. HOUSTON,
Secretary of Agriculture.

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THE EFFECT OF HEAT ON HAWAIIAN SOILS.

INTRODUCTION.

Heat as a means of stimulating crops has been made use of in certain European countries for centuries. The burning of moorlands and the paring and burning of heavy clay sods were extensively practiced in times past. Although their use at present is by no means as common as formerly, these practices have not been entirely abandoned. The adoption of more intensive methods of farming, the use of fertilizers, cost of fuel, recognition of the serious destruction of the organic matter, and the demand for a more continuous use of the land have brought about the gradual disuse of these ancient practices.

In America soil burning, in the sense it is understood in Europe, has never been made use of extensively. In connection with certain crops demanding early forcing, however, soil burning is practiced well-nigh universally. The seed of tobacco, cabbage in some localities, and some other crops that are grown from transplanted seedlings are still sown in soil which has been previously burned. In preparing seed beds for tobacco the soil is frequently burned heavily, usually a strong wood [1] fire being maintained on the bed for several hours. It is a matter of common observation that the growth of seedlings on the burned soil is usually superior to that on the surrounding unburned land. The effects of burning are by no means confined to the germination and growth of seedlings. In newly cleared lands crops of various kinds usually grow more rapidly and produce increased harvests on the spots where brush or log heaps have been burned, and often the effects persist through two or more years.

In Hawaii the growth of certain crops is enormously influenced by the mere burning of small accumulations of brush and undergrowths of guava and lantana. The effect on cotton on the uplands of Oahu produced by these small fires may represent the difference between success and failure. The color and vigor of the crop on these small areas dotted here and there over a field attract attention. Other crops are affected similarly.

[1] Oil and gas are sometimes used for this purpose.

It has been known for a long time that burning improves the structure of clays by causing a coalescence of the smaller particles into larger granules, thus effectively improving the drainage. The increased size of the pores and air spaces within the soil permits of better aeration and encourages deeper root development. By means of heat the hydrous compounds become dehydrated, plasticity and adhesiveness are overcome, the movement of soil moisture facilitated, and a more congenial environment for root development is produced. If sufficiently great heat be employed, the clay may be baked into hard lumps, which yield to cultural and weathering influences with difficulty, and, therefore, injury may result. In any event the dehydrated silicates and oxids return very slowly to their former state and the crumb structure induced by the heat persists for years. The physical effects of heat on clays are so pronounced that the admixing of a few tons per acre of the burnt with the natural soil was formerly employed in Europe as a means of ameliorating heavy clay lands.

Regarding the chemical effects of burning it is also well known that clay soils undergo chemical changes. In general the solubility of aluminum and potassium in acids is greatly increased up to a certain temperature, beyond which a decrease sets in. It is generally held that under the influence of high temperatures, especially with the aid of oxidizing conditions, a wasteful destruction of soil organic matter and consequent loss of nitrogen takes place.

In addition to the above-named physical and chemical effects the killing of weed seeds, parasitic fungi, disease-producing organisms, and insects are generally looked upon as being among the beneficial effects of soil burning.

While the old system of burning the soil has gradually fallen out of use, the closely related partial sterilization by means of heat and volatile antiseptics is of great interest at the present time. In greenhouse work steam sterilization finds extensive application and has been the subject of interesting investigations during the past few years. Likewise the action of dry heat in its relation to partial sterilization and in comparison with the effects of volatile antiseptics on subsequent biological activities has received considerable study. The old idea of considering the subject in a restricted physical and limited chemical sense is, therefore, giving way to a broader view of the question. The more specific chemical effects involved, including certain physico-chemical effects dealt with more in detail in this paper, and the biological results are now being studied.

It has been found that moderate temperatures bring about an increase in the solubility not only of the mineral constituents of soils but also in the organic matter. Furthermore, a number of investigators have found that steam sterilization, particularly when under

pressure, frequently produces a condition that is toxic both to the germination and the subsequent growth of plants. Usually the toxic condition is of short duration and the growth of crops seems to aid effectively in overcoming it. There are many phases of this question that are not fully understood.

There are two characteristics of Hawaiian soils that give them special interest in this connection, (1) the peculiarities and the high proportion of the clay; (2) the inertness of the unplowed and unbroken sod lands. The former gives special interest to the question of heating from the physical point of view, and the latter is of interest to the question because of its bearing on soil aeration. With but few exceptions it is necessary to plow the land, following with thorough tillage at frequent intervals for several months before planting. A field plowed for the first time, although the soil be thoroughly pulverized and reduced to a state of fine tilth, usually will not support plant growth satisfactorily. The farmers of Hawaii have found it necessary to aerate newly plowed lands for a period of several months before planting the first crop. It has been observed, however, that excellent growth of crops is obtained on the small spots where brush was burned and without the continued aeration above referred to. Heat, therefore, seems to accomplish in the soil effects similar to those brought about by aeration. The application of fertilizers produces no such effects.

In connection with a general study of soil aeration the authors have, therefore, been led to a study of the effects of heat on these soils. The present paper deals with one phase of this question, the physico-chemical changes produced. In the first part are presented the data obtained with reference to the solubility of the inorganic constituents and in the second part are some data of a more or less empirical nature on the grosser effects of heat on soil nitrogen.

THE EFFECTS OF HEAT ON THE SOLUBILITY OF INORGANIC CONSTITUENTS.

While a considerable number of investigators have studied the question of the effect of heat upon the solubility of phosphoric acid, using various solvents, apparently few have gone beyond this and determined its effect upon the solubility of the remaining mineral constituents commonly occurring in soils. In fact, with few exceptions, the entire stress has been laid upon the three elements generally considered to be of greatest plant-food value, namely, nitrogen, phosphoric acid, and potash.

In most instances the results of these earlier investigations have shown an increase in solubility of phosphoric acid, with increase in the temperature to which the soils have been heated. M. Nagaoka,[1] on

[1] Bul. Col. Agr., Tokyo Imp. Univ., 6 (1904), No. 3, p. 263.

igniting soils for 15 minutes to remove humus, found an increase in solubility of phosphoric acid, which, he concluded, was due to the destruction of organic matter with which the phosphoric acid was combined. He used as solvents, hydrochloric acid, specific gravity 1.15, distilled water, and several of the weaker organic acids. Stewart[1] used Schmoeger's method of determining the increase of solubility in 12 per cent hydrochloric acid before and after ignition, as an indication of the phosphoric acid combined with organic matter. Fraps,[2] while finding an increase in the solubility of phosphoric acid on ignition, considers that this increase is not wholly due to organic phosphorus, but that mineral phosphates in soils are also rendered more soluble by ignition, thereby rendering the ignition method an unsuitable one for determining organically combined phosphorus. On the other hand, Lipman[3] found while working on a series of California soils, that heating decreased the solubility of phosphoric acid in strong nitric acid. Peterson[4] found that the solubility increased rapidly with increase in temperature from 130° up to 200° C., but that the solubility of the mineral phosphates in soils was not increased by heating below 240° C.

Valuable work on the solubility of the mineral constituents of soils is to be found among the publications of the Bureau of Soils, the work being confined largely to the use of water as solvent. In a bulletin of that bureau,[5] King gives comparative results of work upon fresh and oven-dried soils which show the effect of heating to 110° C. to be striking. On the average more nitrates, phosphoric acid, sulphates, bicarbonates, and silica were recovered from the oven-dried soils than from the fresh samples, while the average of the chlorin determinations showed a decrease. No determination of the basic constituents are tabulated, but King states that upon later investigations he found an increase in potash, lime, and magnesia in oven-dried soils. He makes several suggestions as to the cause of this increase, both from a physical and chemical standpoint, but it is evident from his discussions that he considered the cause to be primarily physical. A number of other investigators have noted an increase in total inorganic matter soluble in water[6] as a result of heating, but no separation of the elements was made.

The special phase to which this paper is devoted is that of the effect of heat upon the solubility of the mineral constituents, distilled water and fifth-normal nitric acid being used as solvents.

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[1] Illinois Sta. Bul. 145.
[2] Texas Sta. Bul. 136.
[3] Jour. Indus. and Engin. Chem., 4 (1912), No. 9, p. 663.
[4] Wisconsin Sta. Research Bul. 19.
[5] U. S. Dept. Agr., Bur. Soils Bul. 26, p. 55.
[6] New York Cornell Sta. Bul. 275.

The results of some preliminary experiments on three Hawaiian soils dealing with the various methods of preparing soil extracts with distilled water are presented in the following table:

Influence of state of moisture and time of extraction on composition of the water extract of soils.

[In parts per million of dry soil.]

	Length of extraction.	Bicarbonates (HCO_3).	Iron oxid and alumina (Fe_2O_3 and Al_2O_3).	Phosphoric acid (P_2O_5).	Manganese oxid (Mn_3O_4).	Lime (CaO).	Magnesia (MgO).	Sulphuric acid (SO_3).	Potash (K_2O).
Soil No. 313:									
Fresh	1 hour	155.0	53.5	2.03	2.55	122.2	62.7	247.0	133.0
Air dried	do	1,040.0	8.7	1.95	17.4	121.8	103.0	120.0	256.0
Oven dried	do	358.0	12.8	2.35	.....	197.0	159.0	194.0	143.0
Fresh	24 hours	95.6	17.8	2.55	2.55	148.0	77.6	257.2	226.6
Air dried	do	678.0	13.0	1.74	15.20	86.8	102.0	134.5	213.0
Oven dried	do	246.0	19.2	3.42	.....	120.0	126.2	199.0	121.0
Fresh	7 days	191.0	45.8	2.55	15.2	96.9	68.3	221.5	239.8
Air dried	do	562.0	44.5	2.38	88.9	160.5	168.0	171.0	282.0
Oven dried	do	262.0	49.1	3.00	.....	102.2	116.0	145.0	61.0
Subsoil No. 314:									
Fresh	1 hour	97.8	38.6	2.32	2.5	56.5	14.8	114.0	150.5
Air dried	do	708.0	4.3	1.94	27.4	77.2	105.2	81.0	142.0
Oven dried	do	371.0	.....	.....	.....	89.0	99.8	145.0	64.1
Fresh	24 hours	117.7	43.7	2.32	5.1	77.0	39.0	175.6	208.5
Air dried	do	651.0	10.8	2.14	30.1	43.0	88.5	72.0	181.0
Oven dried	do	228.0	14.8	2.96	.....	85.0	113.5	131.0	118.0
Fresh	7 days	157.0	23.2	2.05	12.8	71.9	70.4	137.1	227.0
Air dried	do	688.0	6.4	2.14	17.2	47.2	76.1	83.8	158.2
Oven dried	do	180.0	17.0	2.76	.....	63.8	109.0	151.0	68.0
Soil No. 319:									
Fresh	1 hour	140.0	3.04	.76	1.52	127.6	60.2	137.1	142.2
Air dried	do	975.0	20.2	1.80	15.70	224.0	120.0	105.5	278.0
Oven dried	do	558.0	11.2	7.05	.....	194.1	119.5	136.0	135.0
Fresh	24 hours	200.0	4.6	1.37	4.6	197.6	105.1	133.7	170.8
Air dried	do	1,300.0	40.5	1.80	15.7	103.2	81.5	67.2	274.0
Oven dried	do	270.0	15.4	3.31	.....	123.5	103.5	133.0	70.5
Fresh	7 days	99.0	10.3	1.06	7.6	206.7	55.0	155.6	155.0
Air dried	do	1,280.0	9.0	2.02	29.2	162.0	102.0	93.1	234.0
Oven dried	do	485.0	.....	.....	.....	212.0	124.0	159.0	147.0

The soils chosen were from the Koolaupoko district, on Oahu, No. 313 being a sample of brown ferruginous clay soil which occurs widely distributed in this district. It was very dry at the time of sampling and was covered with a heavy growth of guava. No. 314 is the subsoil to No. 313, and No. 319 is a sample of a similar type which had been plowed and planted to pineapples.

The extracts were made by treating the soils with distilled water in the proportion of 5 parts of the latter to 1 of the former in glass-stoppered bottles, shaking occasionally during the period noted in the table, each being shaken an equal number of times. The values are figured to parts per million of the oven-dry soil. Sample No. 313 contained, originally, 18.65 per cent moisture, No. 314 19.65 per cent, and No. 319 30.3 per cent.

It will be seen that in every case the air-dried soil contained the largest amount of soluble HCO_3, the oven-dried sample next, and the fresh soil the least, regardless of the time of extraction.

No attempt was made to separate iron oxid and alumina, but the determination seems to vary considerably in the different soils. No. 313 apparently increased in solubility with increase in time of extraction. If the abnormal figure, 53.5, be disregarded, the difference between the fresh, air-dried, and oven-dried soil is very slight. In the subsoil air drying produced a decrease in solubility, but the oven-dried were more soluble than the air-dried samples. The results from No. 319 are discordant, but indicate the air-dried form to be the most soluble.

Phosphoric acid.—This series is remarkably concordant and indicates an increase in solubility of this constituent upon drying in the oven and at the same time, without exception, shows an increase in solubility with increase in time of extraction.

Manganese.—These results indicate an increase in solubility of manganese with increase in time of extraction and also an increase in solubility upon drying. Unfortunately the whole series of manganese determinations on the oven-dried samples was lost through accident.

Lime.—While the results from the lime determinations are very inconsistent, the general average tends to show an increase in solubility upon heating in the oven and a maximum solubility in the one-hour period of extraction. This latter may be due, however, to subsequent precipitation in the longer extractions.

Magnesia.—The table shows a marked consistency, especially with reference to the rate of increase in solubility of magnesia, due to drying. The concentration of the extracts from the fresh soils was least, with only one exception, while that from the oven-dried soils was greatest in most instances. While there is considerable variation, the data indicate the most complete extraction in that of seven days' duration.

Sulphuric acid.—The relative amounts of this constituent extracted show it to be slightly more soluble in the fresh soil, judging from the average of the series, although only slightly more so than in the oven-dried soil, and that the concentration is practically the same for the several periods of extraction.

Potash.—The potash series shows this element to be much more soluble in the air-dry and fresh soils than in the oven-dried soils, while there is scarcely any difference in the solubility as induced by increasing the time of extraction from 24 hours to 7 days.

The above results tended to establish the advisability of an arbitrary extraction of not over 24 hours, and partly for this reason it was decided that the method at present in general use, namely, shaking for a period of 1 hour and allowing to settle for 24 hours would be suitable to our conditions. Owing to the mechanical texture of Hawaiian soils, caused by the presence in them of highly ferruginous clays, which assume a colloidal form if worked when too wet, it was found necessary to allow the extracts to settle and in every instance, except when heated to 250° C. or ignited, it was necessary to add a

coagulant. Not having the apparatus to effect a rapid filtration through clay filters, small amounts of ammonium chlorid were used to bring about coagulation of the clay and make filtration through filter paper possible. In addition to using distilled water as a solvent, fifth-normal nitric acid was chosen in order to gain additional information concerning the action of different solvents. The means chosen for drying the soils were in an air bath at 100° C., and 250° C., over a Bunsen burner. It being practically impossible to obtain ignition all the samples fresh, extraction upon the soils in this state was not attempted.

METHOD OF PREPARING EXTRACTS.

The soils were prepared as follows: Upon receipt in the laboratory they were spread out to dry. After reaching an approximately stable moisture content portions were weighed into porcelain dishes. One series was dried in an oven at 100° C. for 8 hours continuously, another treated likewise at 250° C., while the last series was heated over a Bunsen burner, at first carefully on a wire gauze for 2 hours to prevent dusting and then over the direct flame for 2 hours, thus destroying practically all the organic matter.

Water extract.—This extraction was made by treating 200 gram portions of the soils with 1 liter distilled water, shaking occasionally for 1 hour, as previously mentioned, and then allowing to settle 24 hours, adding small amounts of ammonium chlorid as a coagulant when necessary. Particular attention was given to these extractions in order that all the samples in each series of the same soil should receive similar treatment as regards the number of times of shaking, thus making the results more directly comparable. Likewise, all distilled water for a series was taken from the same lot in order to eliminate any slight influence which varying amounts of carbon dioxid in the distilled water would have upon the solubility of the minerals. After settling 24 hours the solution was filtered through double filter papers and from this solution 500 cubic centimeters was evaporated to a small volume and used for analysis. All determinations were made gravimetrically except phosphoric acid, iron, and bicarbonate. The former was made colorimetrically in 50 cubic centimeters of the original solution.[1] Iron was determined colorimetrically[2] in a solution of the ammonia precipitate from the 500 cubic centimeters portion, and bicarbonate was determined by titrating 50 cubic centimeters of the original solution with twentieth-normal acid potassium sulphate, using methyl orange as indicator.

Nitric acid extract.—The soils for this phase of the work were prepared in the same manner as above described as regards tempera-

[1] U. S. Dept. Agr., Bur. Soils Bul. 31, p. 45.
[2] U. S. Dept. Agr., Bur. Soils Bul. 31, p. 38.

tures and time of heating. However, in this work only 100 grams were treated with 500 cubic centimeters fifth-normal nitric acid. The extraction differed in that the soils were shaken occasionally, for a period of 5 hours, and then filtered directly through double filter papers. All determinations were made gravimetrically in 100 cubic centimeters of this filtrate with the exceptions of iron, which was determined volumetrically, and phosphoric acid and titanium, which were determined colorimetrically in 25 cubic centimeter portions of the original extract.

SOIL TYPES.

The types of soil selected for this work were of the widest possible range, and represented, in a general way, the normal and abnormal types, both physical and chemical, to be found in the islands. The following table gives the chemical analyses of samples as determined with hydrochloric acid of specific gravity 1.115:

Chemical analyses of soils used.

	Soil No. 74.	Soil No. 164.	Soil No. 9.	Soil No. 292.	Soil No. 290.	Soil No. 405.	Soil No. 416.	Soil No. 417.	Soil No. 406.	Soil No. 428.	Soil No. 426.	Soil No. 448.
	P. ct.	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
Moisture (H_2O)	25.46	1.22	5.36	7.65	8.44	8.02	6.17	16.26	10.34	14.94	10.47	16.00
Volatile matter	13.08	3.56	16.78	8.42	15.80	12.50	17.73	17.53	17.73	22.24	18.28	25.58
Insoluble matter	32.69	48.17	31.67	38.49	40.02	39.12	36.09	30.92	37.31	34.99	24.80	15.10
Iron oxid (Fe_2O_3)	10.13	30.58	18.60	16.63	16.41	15.24	13.20	11.24	10.92	8.24	22.52	19.20
Alumina (Al_2O_3)	12.59	3.05	14.67	12.85	14.11	20.54	20.39	19.38	20.20	10.73	19.10	16.64
Titanium oxid (TiO_2)	.....	1.72	.68	2.00	1.50	2.40	1.60	1.40	1.80	3.20	3.80	4.20
Manganese oxid (Mn_3O_4)	.13	.10	9.21	.24	.30	.15	3.84	2.85	.06	.20	.22	.06
Lime (CaO)	2.63	.12	1.32	1.84	.77	.86	.33	.21	.48	1.91	.15	.50
Magnesia (MgO)	1.09	1.22	.52	8.71	1.30	.99	.44	.36	.67	2.24	.44	1.80
Potash (K_2O)	.14	.48	.79	.39	.17	.20	.39	.45	.20	.24	.28	.15
Soda (Na_2O)	.34	1.46	.38	1.36	.42	.48	.59	.36	.48	1.40	.74	.68
Sulphuric acid (SO_3)	.22	.44	.15	.08	.10	.33	.35	.43	.30	.45	.39	.53
Phosphoric acid (P_2O_5)	1.02	.08	.20	.57	.27	.44	.20	.24	.48	.22	.19	.29

No. 74 is a yellowish-brown soil from Waimea, Hawaii, of sandy silt texture, with an abnormally low clay content, and maintains a very loose, open structure.

No. 164 represents a peculiar type of soil more or less scattered over the islands, which upon absolute analysis shows about 20 per cent of titanium oxid. It is high in iron and aluminum, and also contains a larger percentage of ferrous iron than any of the soils examined heretofore. It has a high specific gravity, bluish-gray color, packs quite closely, has a "clayey silt" texture, and contains an abnormally low content of moisture and organic matter.

No. 9 is a sample of the highly manganiferous type found in the Wahiawa district on Oahu. It has a chocolate-brown color, a sandy silt texture, and maintains an excellent mechanical condition, thus permitting good aeration.

No. 292 represents the type of soil occurring in the lowlands in and about Honolulu now being used for bananas, rice, and truck farming. It has a sandy texture, grayish-brown color, and abnormally high magnesia content.

No. 290 is a peculiar type of soil occurring in the valley on the experiment station grounds, and is undoubtedly of sedimentary origin, its nature being largely determined by washings from the mountain. It is a blue clay soil, exceedingly plastic when wet, but upon drying forms hard compact lumps, and is somewhat similar to adobe or gumbo soils. This soil also has a soapy feel, and during the rainy season aeration and drainage are almost impossible.

Nos. 405 and 406 are samples of a silty soil, to be found in the Kalihi district of Honolulu, which is being used for aquatic agriculture, the former for rice, the latter for taro culture.

Nos. 416 and 417 represent the type of red clay soil which is so abundant on all the islands. These samples were taken only a short distance apart with the view in mind of determining the effect of cultivation, 416 being a cultivated soil, while 417 is practically the same soil from the unbroken sod.

No. 428 is a sample of highly organic, dark-colored soil from Glenwood, Olaa district, Hawaii. It has a very sandy texture and is subjected to heavy rainfall and good drainage, but for some reason, probably climatic, is unproductive.

No. 426 is a sample from Kealia, Kauai, and represents a brown type of soil which has partly undergone a recementation of the particles into a yellow soft rock, hence the sample contains considerable gravel.

No. 448 represents the type of yellow clay scattered throughout the islands in certain districts, this sample having been taken from near Hilo, Hawaii.

The relative solubility of the various constituents is shown separately in order to bring out more clearly the effects of heat, one table being devoted to each element.

SILICA.

The following table shows the results obtained in the study of the effect of heating on the solubility of the silica:

Solubility of silica in water and fifth-normal nitric acid.

[Calculated on basis of dry soil.]

Soil No.	Soluble in water (parts per million).				Soluble in fifth-normal nitric acid (per cent).			
	Air dry.	Dried at 100° C.	Dried at 250° C.	Ignited.	Air dry.	Dried at 100° C.	Dried at 250° C.	Ignited.
74	35.3	13.0	8.7	8.7	0.196	0.187	0.113	0.225
164	10.0	2.0	3.0	4.0	.007	.006	.027	.067
9	8.5	9.5	8.5	7.4	.115	.091	.084	.190
292	4.2	8.3	7.2	10.3	.162	.580	.616	.523
290	2.2	2.1	17.2	8.6	.150	.148	.264	.596
405	2.3	3.9	5.7	16.1	.180	.219	.240	.267
416	12.5	7.8	7.8	10.4	.065	.055	.077	.192
417	2.4	10.5	9.4	22.3	.076	.076	.097	.206
406	4.6	4.5	31.2	33.5	.165	.173	.301	.292
428	15.9	14.9	8.9	11.9	.289	.261	.202	.329
426	1.15	3.38	7.9	1.13	.024	.009	.062	.158
448	0.0	0.0	0.0	8.0	.211	.226	.077	.327

The results of the silica determinations in the water extract are rather inconsistent, but the average shows the highest solubility at ignition. It will be observed that the data obtained with fifth-normal nitric acid disclose some very interesting facts which show that an increase in solubility of silica in dilute nitric acid in Hawaiian soils is produced upon heating to ignition. Furthermore, the tendency points toward a general increase in solubility with increase in temperature. Attention is called to the fact that the soils high in magnesia show the greatest solubility of silica in dilute nitric acid. An exception in this particular is found in sample No. 164, a soil almost devoid of organic matter and containing a very high titanium, iron, and silica content. A further discussion of these results will be taken up following the table of alumina determinations in consideration of the relation of these two elements in the soil.

ALUMINA.

The following table shows the results obtained in the determinations of alumina in heated and unheated soils:

Solubility of alumina in water and fifth-normal nitric acid.

[Calculated on basis of dry soil.]

Soil No.	Soluble in water (parts per million).				Soluble in fifth normal nitric acid (per cent).			
	Air dry.	Dried at 100° C.	Dried at 250° C.	Ignited.	Air dry.	Dried at 100° C.	Dried at 250° C.	Ignited.
74	11.1	3.2	10.3	22.3	0.291	0.292	0.318	0.956
164	7.5	9.5	9.5	5.0	.060	.048	.139	.288
9	4.8	1.1	9.5	3.7	.583	.675	.676	1.034
292	16.6	17.6	14.5	17.1	.874	.598	.584	1.055
290	19.1	12.7	12.8	17.7	.266	.292	.691	.749
405	7.6	13.8	17.6	12.2	.169	.133	.444	.897
416	17.6	12.8	16.1	20.9	.420	.509	1.057	1.515
417	15.3	9.0	4.8	28.9	.679	.661	1.413	1.495
406	10.3	19.6	28.5	38.0	.295	.314	.882	1.425
428	4.4	6.3	11.9	8.8	2.261	2.031	2.208	2.244
426	2.9	6.6	1.7	2.1	.308	.347	1.192	1.571
448	4.9	.7	5.8	2.6	.979	1.757	1.966	2.757

It will be observed from this table that the alumina is affected in very much the same way as the silica. The results, while somewhat inconsistent, show an increase in water-soluble alumina in the heated soils, the number showing increase of alumina by heating from 100 to 250° C., being about the same as in passing to ignition. The effect of heat upon the solubility of this element in dilute nitric acid is very marked and increases regularly with increase in temperature. There is scarcely any correlation between the solubility of the alumina and the total amount of silica present. However, it is worthy of note that there seems to be a relation between the solubility of the alumina in dilute nitric acid and the volatile matter (organic matter and combined water) existing in the soil, as will be readily seen from the

table. Soil No. 164 is almost devoid of organic matter and combined water and contains the least soluble alumina, while, on the other hand, those soils in which the volatile matter is highest contain the most soluble alumina, this being especially noticeable in soils Nos. 428 and 448.

The effect of heat upon the solubility of alumina and silica, especially in water, is probably referable to a number of causes. It is believed, however, to be primarily physical, being related to an alteration of the films surrounding the soil particles and to a modification of the colloidal forms which these elements probably assume under the prevailing conditions. The former effect will be discussed in greater detail farther on. Dehydration and certain chemical alterations at the higher temperatures would, on the other hand, tend toward increasing the solubility in acids through the action of heat upon the hydrated silicates. It has long been known that certain aluminum silicates become more soluble in acids as a direct effect of heat. In the early manufacture of alum advantage was taken of this fact.

IRON.

The relative amounts of iron (Fe_2O_3) recovered by the two solvents appear in the following table:

Solubility of iron in water and fifth-normal nitric acid.

[Calculated on basis of dry soil.]

Soil No.	Soluble in water (parts per million).				Soluble in fifth-normal nitric acid (per cent).			
	Air dry.	Dried at 100° C.	Dried at 250° C.	Ignited.	Air dry.	Dried at 100° C.	Dried at 250° C.	Ignited.
74	17.6	9.7	9.2	12.5	0.003	0.002	0.006	0.055
164	3.5	3.5	3.5	5.1	.005	.007	.083	.047
9	3.7	5.3	3.9	4.5	.007	.016	.006	.006
292	2.9	5.3	3.1	3.5	.194	.037	.037	.013
290	4.8	3.2	4.4	1.8	.069	.069	.142	.046
405	6.4	9.2	5.4	5.1	.324	.302	.290	.157
416	2.8	2.8	2.8	2.5	.032	.032	.027	.015
417	5.2	2.7	3.3	3.8	.026	.029	.029	.033
406	4.6	2.7	4.0	2.1	.515	.487	.333	.158
428	1.9	2.7	3.2	1.6	.024	.033	.039	.107
426	1.7	1.3	1.6	1.3	.037	.061	.014	.082
448	2.1	3.2	2.3	2.1	.051	.038	.077	.024

Again, there is considerable inconsistency in the results, but an average shows the solubility of iron in water to be greatest in the air-dried soil. The solubility in dilute nitric acid is much less consistent than that in water, thereby making it impossible to advance any conclusions except to call attention to the fact that the alumina in Hawaiian soils is very much more soluble, both in water and in dilute nitric acid, than is the iron. But if the results from samples Nos. 292, 405, and 406 be disregarded, and this is plainly permissible since these soils are used in aquatic agriculture and the major part of the soluble iron is in the ferrous condition and would be oxidized

to the ferric condition on being heated to higher temperatures, thus becoming less soluble, then the figures show a marked increase in solubility of the iron with increase in temperature. It will be noticed that the three soils which it is proposed to disregard in drawing conclusions show a markedly regular decrease in solubility of the iron from the air-dried to the ignition state. A qualitative test of the water extract from these three soils showed a very high concentration of ferrous iron from the wet and air-dry samples. In several of the samples in the series there is a close correlation between the effects of the heat on iron and alumina, but it is by no means general.

Iron, alumina, and silica are apparently the constituents least soluble in water. The greater solubility of iron in the air-dried soil may be explained by the fact that the normal mechanical condition of Hawaiian soils is conducive to reducing conditions which result in the formation of small quantities of ferrous compounds. Hawaiian soils, although characteristically basic, normally give an acid reaction, due indirectly to the high clay content and its accompanying poor aeration. Magnification of this condition is to be found in the rice and taro soils, as will be shown in a later table (p. 24), in which soluble iron is found in comparatively large amounts. In such cases it is to be expected that the direct effect of heat would be to oxidize the iron and thus render it less soluble. Further confirmation of this theory is found in the cultivated and uncultivated soils (Nos. 416 and 417, respectively), in which the iron content of the latter is shown to be the more soluble. After heating at 100° the solubility in many instances is greater than in the air-dry samples and is probably due to physico-chemical effects upon the soil films and hydrated silicates. These latter effects are also responsible for the increased solubility of iron in dilute nitric acid as a result of heat.

MANGANESE.

The results obtained from the manganese (Mn_3O_4) determinations are shown in the following table:

Solubility of manganese in water and fifth-normal nitric acid.

[Calculated on basis of dry soil.]

Soil No.	Soluble in water (parts per million).				Soluble in fifth-normal nitric acid (per cent).			
	Air dry.	Dried at 100° C.	Dried at 250° C.	Ignited.	Air dry.	Dried at 100° C.	Dried at 250° C.	Ignited.
74	26.5	30.4	30.4	30.4	0.063	0.041	0.217	0.071
104	9.0	11.0	10.0	9.0	.003	.008	.013	.006
9	23.5	26.5	25.5	20.1	.494	.669	1.692	1.129
292	5.2	4.1	41.4	14.5	.070	.098	.106	.067
290	29.4	20.4	40.8	45.1	.049	.076	.115	.118
405	5.9	10.3	14.9	18.4	.062	.062	.047	.041
416	2.2	4.5	14.4	14.8	.349	.529	1.314	.739
417	15.7	38.7	180.5	219.2	.385	.580	1.052	.748
406	9.1	4.4	6.0	9.6	.035	.030	.048	.040
428	15.9	161.1	32.8	6.3	.094	.102	.225	.135
426	6.9	9.0	90.3	33.8	.004	.012	040	.023
448	2.8	13.4	108.7	119.6	.028	.032	.126	.050

This table shows that the solubility of manganese in water is much greater in the heated soils, being most soluble in the ignited samples. The surprising feature of this table is the fact that several of the soils in the series show manganese in a much more soluble form than the manganiferous soil containing 9.21 per cent total Mn_3O_4. A possible explanation is found in the results upon the cultivated and uncultivated soils (Nos. 416 and 417, respectively), namely, that cultivation and the accompanying aeration has the effect of producing a lower state of oxidation or other changes which render the manganese less soluble in water. An observation of Nos. 416 and 417 (cultivated and uncultivated) shows a large decrease in solubility as a result of cultivation, and the highly manganiferous soil (No. 9) has been in cultivation for some time.

The table showing the solubility of manganese in dilute nitric acid presents a remarkably consistent series of results, as is shown by the increase in solubility as a result of the action of heat up to 250° C., followed by a large decrease as effected by ignition. This is true with only two exceptions in the entire series.

It is difficult to explain the effects of heat upon the solubility of manganese. This element occurs in some Hawaiian soils as concretions, especially in the highly manganiferous soils, and is present, at least partially, as manganese dioxid. But in the normal types concretions are absent, and here the manganese probably exists largely in a lower state of oxidation, and hence in a more soluble form. In any case manganites and salts may occur to a limited extent. As already noted, the soils heated to 250° C. and ignition gave the more concentrated water extract, an average indicating the maximum concentration from the ignited soils. The effect of heat upon the physical properties is probably the prime factor which influences the solubility in water. With one exception the oxids of manganese are quite insoluble in nitric acid, this oxid being manganous oxid (MnO). Therefore the higher oxids, such as manganomanganic oxid (Mn_3O_4) and manganic oxid (Mn_2O_3), which are both essentially combinations of manganese dioxid and manganous oxid,[1] are soluble in nitric acid to the extent of their MnO content, while their MnO_2 content remains insoluble. Consequently the solubility of manganese oxids increases with increase in heat owing to the above-mentioned decrease in state of oxidation, as high temperatures convert MnO_2 into Mn_3O_4 and Mn_2O_3, each of which is partially soluble in nitric acid. Therefore heat would tend to increase the solubility in nitric acid of that portion occurring as MnO_2.

In addition, it is known that the action of heat upon organic compounds of manganese and also certain of its salts converts them into

[1] $Mn_3O_4 = 2\,MnO + MnO_2$; $Mn_2O_3 = MnO + MnO_2$. Hence it may be observed that Mn_3O_4 contains the more soluble manganese.

oxids. Then, apparently the more soluble oxid, Mn_3O_4, is formed in greater amounts when the soil is heated to 250° C.

LIME AND MAGNESIA.

The two tables below show the effects of heat upon the solubility of lime and magnesia:

Solubility of lime in water and fifth-normal nitric acid.

[Calculated on basis of dry soil.]

Soil No.	Soluble in water (parts per million).				Soluble in fifth-normal nitric acid (per cent).			
	Air dry.	Dried at 100° C.	Dried at 250° C.	Ignited.	Air dry.	Dried at 100° C.	Dried at 250° C.	Ignited.
74	176.8	330.6	2,801.1	1,039.5	2.312	2.332	2.131	1.427
164	28.1	44.2	64.3	38.1	.026	.030	.024	.024
9	224.9	302.9	910.9	766.8	.448	.909	.511	.323
292	112.6	86.9	242.3	207.1	.147	.856	.986	.674
290	183.0	232.1	195.6	206.3	.378	.406	.318	.876
405	296.9	133.3	363.0	261.9	.344	.362	.330	.316
416	82.2	107.3	270.6	232.6	.159	.158	.124	.108
417	26.5	98.5	330.5	332.9	.174	.174	.167	.136
406	57.1	93.9	697.5	547.7	.388	.409	.329	.191
428	184.4	1,455.6	1,509.3	220.6	.466	.479	.395	.368
426	16.1	33.8	225.8	106.1	.056	.083	.056	.058
448	59.2	67.1	763.6	708.6	.248	.252	.226	.162

Solubility of magnesia in water and fifth-normal nitric acid.

[Calculated on basis of dry soil.]

Soil No.	Soluble in water (parts per million).				Soluble in fifth-normal nitric acid (per cent).			
	Air dry.	Dried at 100° C.	Dried at 250° C.	Ignited.	Air dry.	Dried at 100° C.	Dried at 250° C.	Ignited.
74	75.1	73.9	182.7	63.1	0.121	0.123	0.138	0.096
164	50.2	42.2	60.2	44.2	.019	.020	.021	.019
9	96.4	99.5	167.3	150.4	.071	.066	.081	.049
292	83.4	91.1	136.7	130.5	.150	.359	.344	.197
290	285.2	385.2	230.3	192.6	.500	.522	.301	.283
405	209.7	130.9	151.6	147.0	.206	.204	.140	.060
416	105.1	127.5	140.9	127.5	.073	.062	.042	.046
417	67.5	126.6	189.8	157.1	.071	.073	.049	.062
406	82.2	87.2	234.7	245.9	.204	.226	.115	.098
428	152.6	366.8	268.4	134.2	.114	.107	.082	.079
426	34.6	47.4	158.1	108.4	.047	.040	.041	.044
448	57.8	77.8	297.9	303.3	.074	.064	.048	.048

The series of lime determinations shows that this constituent is most soluble in water in the soils which were heated to 250° C. and least soluble in the air-dried soils. This is true of every sample except one (No. 290), this latter being a peculiar adobe type of soil from the experiment station grounds. In dilute nitric acid it will be observed that lime is most soluble in those soils heated to 100° C., and, unlike the water extractions, the least concentration is obtained from the ignited soils. Thus it is shown that the action of nitric acid in no way correlates with that of distilled water. However, the results show the more highly organic soil to contain lime

in such form as to be more soluble in weak solvents, No. 164, a mineral soil, being the least soluble. Attention is also called to the effect of cultivation or aeration upon the solubility of lime and magnesia, namely, that the cultivated soils contain these elements in far more soluble form.

From a study of the table of magnesia determinations it is evident that the action of the solvents upon this element is quite similar to their action on lime as regards the effects of heat, but that the lime is very much the more soluble both in water and in dilute nitric acid. The results of the extractions with water show a maximum solubility in the samples heated to 250° C., the least soluble magnesia in the air-dry samples. This exactly correlates with the results of the lime determination. The solubility in dilute nitric acid does not correspond so closely, but the general tendency is similar in that the air-dry samples and those dried at 100° C. contain this element in the highest state of solubility, while in the ignited soils it is least soluble. An important fact to which attention is called is that, although most of the soils in this series show from digestion with hydrochloric acid (1.115 specific gravity) a higher magnesia content than lime, one of them four times as much, yet the lime, with very few exceptions, is considerably more soluble. One exception is to be found in sample No. 290, which represents a soil having a characteristic soapy property indicating the presence of hydrous magnesium silicate.

The effect of heat on the solubility of lime and magnesia is more striking than in case of the other elements. It is highly probable that the increased concentration of the water extract of the soil heated to 100° C. over the air-dried sample is produced through physical causes, namely, destruction of the soil film and dehydration accompanied by a slight decomposition of organic matter. On the other hand, the soil when heated to 250° C. undergoes more completely all the above transformations as well as decomposition of organic matter. Since calcium and magnesium are two of the elements universally combined with organic matter, there necessarily follows an increase in solubility as a result of the more complete decomposition. The soils showing the greatest solubility of these elements in water were those containing the highest organic matter.

The decrease in solubillty of lime and magnesia in water and in nitric acid at 250° C. and ignition is hard to explain. It is undoubtedly partly due to chemical changes in the soluble forms resulting from the decomposition of the organic matter and is also influenced by the decrease in exposed surfaces as a result of an aggregation of the soil particles and probably other physical factors. It is suggested that one of the chemical changes taking place as a result of heat is that of a replacement of the potash and soda in the silicates by

magnesia and lime, more particularly the latter. The data in the tables show a decrease in solubility of lime and an increase in that of potash upon ignition in a majority of the samples. In addition to the above-mentioned factors a decrease in solubility after ignition would be produced by the conversion of the bicarbonates into normal carbonates, the former of which are more soluble than the latter. This would, of course, be most striking in the water extracts.

POTASH.

The following table shows the relative effects of heat upon the solubility of potash:

Solubility of potash in water and fifth-normal nitric acid.

Calculated on basis of dry soil.]

Soil No.	Soluble in water (parts per million).				Soluble in fifth-normal nitric acid (per cent).			
	Air dry.	Dried at 100° C.	Dried at 250° C.	Ignited.	Air dry.	Dried at 100° C.	Dried at 250° C.	Ignited.
74	128.2	117.4	339.3	217.5	0.053	0.066	0.050	0.068
164	64.3	82.3	40.1	132.5	.027	.032	.026	.071
9	117.8	192.7	301.9	260.6	.073	.081	.064	.113
392	77.2	76.3	118.0	83.8	.061	.155	.202	.134
290	87.1	92.4	90.6	77.4	.177	.142	.054	.094
405	96.6	55.1	45.9	43.6	.056	.084	.095	.090
416	98.2	96.2	78.3	147.6	.055	.056	.038	.062
417	60.3	100.8	77.4	140.6	.061	.054	.038	.072
406	36.5	49.2	19.4	78.2	.014	.013	.032	.022
428	244.8	202.8	353.5	220.7	.038	.051	.029	.041
426	43.8	58.7	56.4	182.9	.025	.024	.030	.070
448	119.8	107.4	64.4	59.0	.032	.032	.033	.053

The figures show that the effect of heat upon potash is slightly different from the effects on lime and magnesia. The ignited soils appear to contain this element in the most soluble form, while the samples dried in air and at 100° C. contain it in the least soluble form. In the air-dried samples potash is also more soluble in the cultivated than in the uncultivated soil, and the greatest solubility of this element is also found in the highly organic soils.

Soils in general possess fixing power for potash and for phosphoric acid in particular. The fixing of potash is generally believed to be due to hydrated silicates and organic matter. Cameron and Bell [1] on continuously extracting a soil with water until no more potash dissolved, then grinding the sample and reextracting, found an additional amount of potash to be removed. This they attributed to a colloidal aluminum silicate upon the surface of the particles, thus protecting them from the action of the water as well as absorbing the potash. Dehydration and decomposition would therefore materially overcome the fixing power, and the potash replaced by lime or magnesia would not be refixed during a short period.

[1] U. S. Dept. Agr., Bur. Soils Bul. 30, p. 26.

PHOSPHORIC ACID.

In the next table are shown the results of the action of heat on the solubility of phosphoric acid.

Solubility of phosphoric acid in water and fifth-normal nitric acid.

[Calculated on basis of dry soil.]

Soil No.	Soluble in water (parts per million).				Soluble in fifth-normal nitric acid (per cent).			
	Air dry.	Dried at 100° C.	Dried at 250° C.	Ignited.	Air dry.	Dried at 100° C.	Dried at 250° C.	Ignited.
74	39.8	69.6	58.7	32.6	0.007	0.008	0.024	0.043
164	24.1	36.1	16.1	15.1	.005	.006	.007	.009
9	17.1	44.5	52.9	32.8	.007	.007	.011	.013
292	21.9	26.9	23.8	22.8	.058	.018	.020	.053
290	22.9	36.5	25.8	27.9	.006	.016	.020	.031
405	27.1	31.0	33.0	25.3	.011	.014	.027	.021
416	36.5	43.6	49.2	51.4	.005	.007	.007	.006
417	54.3	52.7	46.8	39.8	.005	.008	.009	.005
406	23.4	35.7	21.2	23.4	.024	.030	.064	.047
428	25.6	38.7	26.8	23.8	.011	.013	.012	.014
426	25.4	24.8	27.1	27.1	.008	.012	.011	.013
448	29.6	36.2	37.6	28.1	.028	.028	.036	.020

It may be seen from this table that the solubility of phosphoric acid is materially affected by heat, the solubility in water being greatest in the soils heated to 100° and 250° C., if it be permissible to draw conclusions from the general averages, while it is least soluble in the air-dried soils. It is also worthy of note that this element is more soluble in the uncultivated than the cultivated soil, the former, however, decreasing with increase in heat. In the extractions made with dilute nitric acid the average indicates a greater solubility in the ignited soils, the solubility tending to increase with increase in temperature.

Phosphoric acid exists in soils in major part combined with iron, aluminum, magnesium, and calcium, and is also found combined with organic matter, being always present in the so-called humus of soils. It may be in the form of basic phosphates, hydrogen phosphates, or as complex phosphates in combination with more than one element. It is probably combined mostly with iron and aluminum and titanium in Hawaiian soils. Considerable work has been done upon the effect of heat upon the solubility of this constituent and several attempts have been made to draw conclusions from these results as to its state of combination; that is, whether organically or inorganically combined. Peterson[1] using fifth-normal nitric acid found that after oxidizing the organic matter with hydrogen peroxid there was no increase in the solubility of phosphoric acid when the soil was heated to 240° C. He concluded, therefore, that the solubility of mineral phosphates in soils is not increased up to 240° C. The author's results tend to indicate a decrease in solubility of phosphoric acid at high tem-

[1] Wisconsin Sta. Research Bul. 19

peratures, due either to a chemical change in its combination to a form less soluble in water or an increase in the absorbing power of the soil. The increase effected at 100° and 250° C. is undoubtedly partly due to destruction of organic matter and to the breaking up of the colloidal film. The action of dilute nitric acid is somewhat different, in that an increase in solubility upon ignition accompanies that of iron, alumina, silica, and titanium. Iron and aluminum in Hawaiian soils occur in the form of hydrates to a certain extent and are more or less impregnated with the phosphoric acid and titanium oxid, not only holding them in chemical combination, but also mechanically. The effect of heat would directly increase the solubility of these constituents in dilute nitric acid gradually up to the point of ignition, at which point the decomposition of the hydrates would be at a maximum. Changes due to the destruction of organic matter would cause an increase in the solubility of this element. Another factor of some importance in this connection is that of precipitation subsequent to solution. The increased solubility of aluminum and manganese would probably produce some precipitation of phosphoric acid, particularly in the water extract.

SULPHATES.

The following table shows the solubility of sulphates (SO_3) as affected by heat:

Solubility of sulphuric acid in water and fifth-normal nitric acid.

[Calculated on basis of dry soil.]

Soil No.	Soluble in water (parts per million).				Soluble in fifth-normal nitric acid (per cent).			
	Air dry.	Dried at 100° C.	Dried at 250° C.	Ignited.	Air dry.	Dried at 100° C.	Dried at 250° C.	Ignited.
74	172.4	130.5	1,961.6	1,309.2	0.027	0.019	0.106	0.067
164	72.3	66.2	206.7	168.6	.037	.031	.027	.025
9	111.4	146.2	1,339.7	1,294.4	.017	.019	.053	.034
292	164.7	159.5	722.5	532.3	.067	.018	.019	.055
290	100.2	176.2	1,128.3	799.5	.022	.026	.062	.063
405	129.6	149.3	942.0	583.6	.018	.016	.067	.048
416	59.4	100.6	702.3	664.3	.028	.035	.038	.041
417	98.9	103.1	872.1	926.0	.032	.032	.037	.052
406	260.3	326.4	1,555.9	1,479.9	.061	.086	.163	.187
428	494.8	2,123.7	2,598.0	680.1	.089	.073	.101	.177
426	46.2	54.2	119.7	241.6	.018	.034	.019	.024
448	110.0	107.4	1,621.3	1,575.7	.028	.029	.044	.122

It will be seen from this table that the effect of heat upon the solubility of the sulphates is quite marked, more so in the water extracts. In this series the air-dried soil is the least soluble, that dried at 100° C. next, while the maximum solubility is reached at about 250° C., decreasing upon ignition. On the other hand, the solubility in dilute nitric acid is slightly different in that the average shows the maximum solubility to be obtained from the ignited samples, the least soluble being in the oven-dried (100° C.) soil. The surprising feature of these results is the markedly greater solubility of sulphates in water than in

nitric acid as shown in a number of instances. This is probably due to precipitation subsequent to extraction in the nitric acid extracts.

Part of the increase in the solubility of sulphates in the heated soils of this series was probably due to absorption of the products of combustion of the gas used in heating the oven. It was found that by passing the products of combustion through water a precipitate of barium sulphate was obtainable upon the addition of barium chlorid. King[1] found an enormous increase in the solubility of sulphates upon heating in an oven at 110° C. using both gasoline and kerosene as a source of heat, thus largely eliminating this factor. In spite of the possibility of an introduction of error due to this cause it is probable that the results tabulated here disclose correctly the effect of heat upon the sulphates. In addition to the already-mentioned reasons, namely, destruction of organic matter, soil films, etc., it is necessary to take into consideration the chemical effect of heat upon the various mineral sulphur compounds. Calcium sulphate is known to exist in four forms, two being anhydrous, one of which is more soluble than the other. Sulphur also exists in soils as sulphids generally combined with iron, or as sulphates in combination with iron, lime, or magnesia, also combined with organic matter in many essential forms. The effect of heat would be most marked upon the latter in that it would undergo considerable decomposition at 250°, the sulphur being oxidized to sulphur dioxid or trioxid, which upon treatment with water as a solvent would tend to form sulphuric acid or sulphates to the extent of the bases in solution. On the other hand, it is evident that large amounts of sulphur will be lost through volatilization upon ignition. Soil No. 428, a highly organic soil, illustrates this effect best in that the increase from air dried to oven dried (100° C.) is 1,600 parts per million, while the decrease from the sample heated from 250° C. to ignition is 1,900 parts per million. It is evident from these data that upon igniting the soils the sulphur set free from the destruction of the organic matter is oxidized and volatilized so that it is lost before combination with the bases takes place.

BICARBONATES.

The following table shows the bicarbonate content of the water extracts:

Solubility of bicarbonates in water.

[Parts per million of dry soil.]

Treatment of soil.	Soil No. 74.	Soil No. 164.	Soil No. 9.	Soil No. 292.	Soil No. 290.	Soil No. 405.	Soil No. 416.	Soil No. 417.	Soil No. 406.	Soil No. 428.	Soil No. 426.
Air dried	370.1	106.4	113.5	158.5	132.9	161.4	35.4	73.6	52.5	73.1	70.5
Dried at 100° C	448.0	137.4	419.4	283.7	202.7	297.5	221.4	286.0	136.4	204.3	102.7
Dried at 250° C	1,309.2	91.3	338.9	363.5	327.7	157.3	153.3	143.0	68.2	582.8	895.4
Ignited	314.2	45.1	230.9	252.1	70.9	174.6	73.8	53.9	118.5	133.1	240.5

U. S. Dept. Agr., Bur. Soils Bul. 26 p. 56.

The results herewith shown are not very consistent, but the average ndicates the maximum solubility of carbonic acid to be in the samples treated to 100° and 250° C., indicating that drying has the effect of increasing the amounts of bicarbonates in the soil and thus increasing the solubility of the bases with which carbonic acid combines. One reason suggested in the above table for a decrease in water soluble constituents upon ignition is that ignition would cause a transformation of the bicarbonates into normal carbonates, therefore temporarily reducing their solubility in water.

At the beginning of this work some determinations of titanium were made, but these were not carried through the series. This element was not present in the water extract in large enough quantities to be determined. In the dilute nitric acid extracts it was present in very small amounts in the samples dried in air and at 100° C., but in much larger quantities in the extracts from samples heated to 250° C. and ignition, the maximum solubility being obtained upon the ignited samples.

EFFECT OF HEAT UPON RICE AND TARO SOILS.

In the following table is shown the effect of heat upon the soils used in aquatic agriculture, comparing this with the solubility of the elements in the wet and soggy condition:

Effect of heat upon soils used in aquatic agriculture.

[Parts per million of dry soil water extract.]

Condition of sample.	Silica (SiO_2).	Alumina (Al_2O_3).	Iron oxid (Fe_2O_3).	Manganese oxid (Mn_3O_4).	Lime (CaO).	Magnesia (MgO).	Potash (K_2O).	Phosphoric acid (P_2O_5).	Sulphuric acid (SO_3).	Bicarbonates (HCO_3).
Rice soil, No. 405:										
Wet	6.9	5.6	12.2	64.7	664.8	438.7	111.9	43.7	153.9	328.9
Air dry	2.3	7.6	6.4	5.9	296.9	209.7	96.6	27.1	129.6	161.4
Dried at 100° C.	6.9	13.8	9.2	10.3	133.3	130.9	55.1	31.0	149.3	297.5
Dried at 250° C.	5.7	17.6	5.4	14.9	363.0	151.6	45.9	33.0	942.0	157.3
Ignited	16.1	12.2	5.1	18.4	261.9	147.0	43.6	25.3	583.6	174.6
Taro soil, No. 406:										
Wet	36.6	62.4	86.1	34.4	318.6	310.0	31.8	38.7	137.8	294.9
Air dry	4.6	10.3	4.6	9.1	57.1	82.2	36.5	23.4	260.3	52.5
Dried at 100° C.	4.5	19.6	2.7	4.4	93.9	87.2	49.2	35.7	326.4	136.4
Dried at 250° C.	31.2	28.5	4.0	6.0	697.5	234.7	19.4	21.2	1,555.9	68.2
Ignited	33.5	38.0	2.1	9.6	547.7	245.9	78.2	23.4	1,479.9	118.5

When the types of soil were chosen for use in this series, two were selected with a view to obtaining some information upon the soils in use for rice and taro culture. It would be expected that heat and its accompanying oxidation would have a marked effect upon this type of soil for the reason that for the most part it exists in a reducing environment. The above table shows solubility in water only. The samples were taken from the field in wet condition and extractions were made upon weighed samples immediately upon receipt in the laboratory, the moisture content in this state being about

50 per cent. This table discloses the high concentration of soluble plant food in these soils under the reducing conditions. While the mineral constituents tend to increase in solubility with increase in heat with relation to the air-dry samples, a maximum solubility is obtained from the wet samples in the case of the iron, manganese, lime, magnesia, phosphoric acid, and bicarbonates, and in one of the samples a maximum solubility is obtained for the remaining constituents, silica, alumina, and potash. Therefore, these results indicate that the effect of drying and heating the soils used in aquatic agriculture does not increase the solubility of the mineral constituents over and above the solubility in the wet state but rather brings about a decrease in all constituents except sulphates.

The concentration of the extracts from these soils in the wet state does not necessarily indicate that the mineral constituents, with the exception of iron, are actually more soluble than those of dry-land soils. Neither should we conclude that the abnormal concentration is wholly due to more complete diffusion coupled with greater solubility induced by the environment to which these soils are subjected. The amount of water always present in these soils is far in excess of that occurring in dry-land soils, and since there necessarily must be a tendency toward constancy in concentration regardless of the amount of solvent present, in time the absolute amounts of solids going into solution would be considerably greater in submerged soils. The moisture content of these two soils when received at the laboratory was about 50 per cent, whereas the dry-land soils contain very much less moisture. The water extracts obtained by the methods employed, therefore, would necessarily contain greater absolute amounts of substances already in solution in the soil water. Hence the concentration of the nutrient solution occurring in submerged soils need not necessarily be greater than that of dry-land soils.

DISCUSSION.

The foregoing results show that an increase in solubility of the mineral constituents of various types of Hawaiian soils is effected by heating. The samples represent most of the normal and abnormal types of the islands. That there are both chemical and physical factors concerned in the phenomena at hand must be admitted at the outset. It is believed, however, that the most important set of factors affecting the solubility of inorganic soil constituents are of a physical nature.

Undoubtedly the means by which the physical factors act is through the soil moisture in its relation to the physical properties of the soil. The conditions conducive to the formation of a colloidal state and the subsequent relation of heat to the destruction of this colloid are two of the most important of these factors.

It is certain that soil moisture distributes itself around the soil particles and in some instances as an impregnation within the particles. The moisture therefore occurs as thin films which, according to certain physical conceptions, must be held around the particle by an enormous pressure. From purely physical considerations this pressure has been estimated at several thousand atmospheres. Under such pressure the concentration of film water with reference to the mineral matter should be much greater than that of the free or capillary water in the soil.

Then the air-dried soil, the particles of which are still surrounded by a film of moisture, when shaken with water, should theoretically show the least solubility. The results reported in this bulletin in most instances are in harmony with this assumption. But if the soil be allowed to remain in the condition and environment prevailing in submerged cultures, that is, in the presence of a large excess of water, then in time diffusion would bring about a more or less equal distribution of dissolved materials throughout the entire water present and the pressure of soil films would be decreased to a minimum or entirely eliminated. Hence the amount of materials going into solution in the free water in such soils would be expected to be abnormally high. Upon air drying such soils the normal films would again appear with a resulting decrease in solubility. Subsequent heating ought then to affect these soils in a way similar to that produced on dry-land soils. The data presented in the previous tables are again in harmony with this view.

Water, however, not only exercises a solvent action on minerals but forms various hydrates, the solubility and physical character of which in some instances are greatly altered; organic as well as inorganic matter goes into solution with the result that the moisture films around the particles became solution films, holding in suspension and more or less intermingled with colloids, both organic and inorganic. The films then may be looked upon as being of a colloidal nature.[1]

Upon heating to 100° C. alterations in the films would take place through evaporation and by partial dehydration of colloids, thus destroying the pressure by which the film was previously held around the particles. At the temperature of 100° C. the concentration of the soil moisture would also be temporarily increased, due to increase in solubility with heat. During the course of the evaporation the concentration of the soil moisture would increase to the saturation point, after which the mineral matter would be deposited on the surface of the film as evaporation went on.[2] Also the materials held in solution in the interior of the permeable particles would be partially deposited

[1] No claim is made for originality in this view. The idea of soil films, colloidal films, etc., has been made use of by various writers on soils.

[2] King (loc. cit.) in discussing the relative solubilities of fresh and dried soils advanced this idea.

on the surface of the water evaporated. Upon adding water to the soil after having been dried, it is probable the materials deposited from previous evaporation would be more soluble than the other mineral constituents. In addition a certain amount of oxidation and other chemical changes in the organic matter might reasonably be expected to take place, which would have some effect on the solubility of the mineral bases that tend to combine with the organic matter.

The solution obtained upon shaking with water a soil previously dried should, in the light of these views, be of a greater concentration than that prepared from the air-dried soil. With the absence of soil films and a more or less altered condition of the colloids present the solvent would have more ready access to the soil particles during a short period in addition to coming into immediate contact with solids deposited on the surface of the particles.

Why several of the mineral constituents of the soil should be so markedly more soluble when heated to 250° C. than at the other temperatures is a question not easily answered. The difference in physical effects were quite noticeable in that there was a greater aggregation of particles. Again, there was a more complete destruction of organic matter effected at this temperature, and also it is not entirely impossible that drying at 100° C. for eight hours does not effect a complete elimination of the soil moisture and especially the water of chemical combination. It seems reasonable, then, that the effects of heating to 100° C. are simply magnified when heated to 250° C. Added to this there is a more complete destruction of organic matter, the effect, both physical and chemical, being of the same general nature but more complete at the higher temperature. The destruction of organic constituents being more complete would necessarily increase the solubility of the mineral matter held in combination, as it is generally conceded that the organic constituents of the soil in its natural state are quite insoluble in water and acids, more especially in the former. There is also evidence of the existence of fatty or resinous organic matter which would materially affect the properties of the soil film. For the decomposition of such bodies it would be necessary to heat the soils considerably above 100° C.

In addition to the above-mentioned effects of heat the relation between solid and solvent would naturally be affected by other factors. Among these is the absorption or "fixing power" of the soil.[1] It is reasonable to expect soils with widely varying physical and chemical properties, such as those used in this series, to differ greatly in absorptive power. Hence it is not at all unlikely that the lack of consistency in some of the results in the foregoing tables is due primarily to this factor. Not only is there lack of uniformity in

[1] Richter (Landw. Vers. Stat., 47 (1896), p. 269) found that heating increased the absorptive power of the soil for water.

the absorptive power of soils, but they also show considerable selective power in the absorption of mineral constituents. Soils high in humus have a high fixing power, due to the ability of humus to combine chemically with minerals, as well as its power of absorption, and therefore the effect of heat upon highly organic soils should tend to increase the solubility of the minerals. An example of this is given in the cases of soils Nos. 74 and 428. Another factor is that of precipitation following extraction, being the more marked in the acid extract due to a more complete extraction.

In passing from 250° C. to ignition the effects are apparently of a specific rather than general nature, as has been already indicated. Among these effects are the volatilization of certain sulphur compounds, conversion of bicarbonates into normal carbonates, dehydration of silicates, etc., replacing of potash by lime, and other chemical transformations. In addition there is produced a greater aggregation of the soil particles, resulting in a decrease in surface area exposed to the solvent and an accompanying change in the fixing and absorbing powers of the soil. It is possible, by application of these conceptions, to explain the majority of changes, both increase and decrease in solubility, resulting from ignition.

THE EFFECTS OF HEAT ON SOIL NITROGEN.

INTRODUCTION.

The data presented in the preceding pages indicate the existence of colloidal films surrounding the soil particles. These films are probably both organic and inorganic in nature and undergo alteration under the influence of heat. By such alteration new surfaces become exposed to the action of solvents, thereby making possible the solution of materials otherwise effectively protected from the solvents used. There is considerable evidence in the data, however, that other changes were also produced by the heating. Some oxidations must have taken place, and probably decompositions of other types. Changes in the organic matter were produced at the higher temperatures, as shown by the color of the water extracts.

The effect of heat on soil organic matter has been the subject of some previous investigation. It has been observed, for example, that water extracts from heated soils are usually darker in color and contain greater amounts of organic matter than similar extracts from unheated soils.

Darbishire and Russell [1] found that plants absorb more nitrogen from soils that have been previously heated to 95° and 120° C. than from unheated soils. They concluded that the heating brought about some decompositions in the organic matter and also caused a modification in the bacterial flora.

[1] Jour. Agr. Sci., 2 (1907), p. 305.

Pickering [1] found that partial sterilization brought about an increase in the solubility of the organic matter. An increase in the total nitrogen soluble in water and greater absorption of nitrogen by plants were also produced by heating.

Lyon and Bizzell [2] observed that the action of steam heat at 2 atmospheres pressure greatly increased the ammonia, in addition to increasing the water soluble inorganic matter. The nitrates were largely decomposed at this temperature and pressure.

Russell and Hutchinson [3] have shown that by heating some Rothamsted soils at 98° C. for three hours a small increase in the ammonia content took place. The most remarkable effect of the partial sterilization, however, was in connection with subsequent ammonification. Ammonia began to be formed in the course of a few days, followed by a remarkable production of ammonia later on. Corresponding to the increase in ammonia subsequent to heating, an enormous increase in the numbers of microorganisms (bacteria and fungi) took place. Heating to 125° also caused an initial production of small amounts of ammonia, but no subsequent ammonification set in. The nitrates were little affected although nitrification was entirely inhibited by the treatment. From the fact that volatile antiseptics bring about similar effects, these authors believe that partial sterilization kills certain biological agents which, in the untreated soil, effectively hold in check the multiplication and activity of the ammonifying organisms. After these inhibiting agents are destroyed the ammonifying efficiency of the soil rises rapidly, thus making available greatly increased amounts of nitrogen.

Lodge and Smith [4] found that decoctions from soils show an increase in ammonia after steam sterilization at 15 pounds pressure, but a decrease in ammonia took place from the sterilization of the subsoil.

Lathrop and Brown [5] found that the amounts of ammonia and total nitrogen soluble in water increased with an increase in the pressure under which the soil was heated. At 10 atmospheres approximately 40 per cent of the total nitrogen was rendered soluble, while the ammonia thus split off was found to vary from 7.83 per cent to 15.64 per cent.

Recently Schreiner and Lathrop [6] published a comprehensive investigation of the effects of steam heat on soil organic matter. In this work they isolated from heated soils a number of compounds not found in the unheated soil. Among the compounds isolated a

[1] Jour. Agr. Sci., 2 (1908), p. 411.
[2] New York Cornell Sta Bul. 275 (1910).
[3] Jour. Agr. Sci., 3 (1909), pp. 111-144.
[4] Massachusetts Sta. Rpt. 1911, pt. 1, pp. 126-134.
[5] Jour. Indus. and Engin. Chem., 3 (1911), p. 657.
[6] U. S. Dept. Agr., Bur. Soils Bul. 89; Jour. Amer. Chem. Soc., 34 (1912), pp. 1242-1259.

number are nitrogenous and it is of special interest in this connection that practically all of these have been found to be beneficial to plant growth. Certain nonnitrogenous bodies, however, were also isolated, one of which, dihydroxystearic acid, seems to have been formed under the action of heat and which has been found to be distinctly toxic to plants.[1] It has been known for some time that steam heat may bring about toxic conditions in soils, apparently of an organic nature, but it remained for Schreiner and Lathrop to determine definitely what is at least one of the toxic bodies thus produced. On the one hand, these authors have shown that definite nitrogen compounds of a character beneficial to plant growth are formed by the action of heat, while on the other, a toxic compound, also organic and definite in character, may be generated at the same time. The significance of these discoveries is at once apparent; the value of such definite and fundamental data can not fail to be important.

A knowledge of the effects of steam heat on soil organic matter has special bearing on greenhouse practices, but may it not well be asked, what are the effects of dry heat without pressure? This phase of the question has not been exhaustively studied. It is unsafe to conclude a priori that the same types of cleavage and hydrolysis take place in the absence as under the influence of pressure. There is evidence in the growth and appearance of crops on burned soil that nitrogen is made available by the heat. The deep green color of the crop is sometimes very striking. It is important, therefore, that this phase of the question be investigated in a general study of soil heating on account of the importance of nitrogen in the nutrition of plants.

In an altogether different connection our attention was drawn to the very large increase in the ammonia of some Hawaiian soils brought about by the action of heat. It was observed that the ammonia content of certain soils increased from a few parts to over 400 parts per million. At the same time the nitrates were decomposed. From these observations and its general bearing on soil heating, an investigation of the nitrogen transformations seemed of interest and importance. Whence the ammonia thus set free and from what class of compound does it arise?

The nitrogen of soils having been at one time bound up in organized tissue, plant and animal, and, therefore, largely of proteid nature, undergoes hydrolysis under the action of enzyms, bacteria, etc., with the resulting formation or splitting off of simpler compounds. In soils there must occur every stage of these changes from the proteid complex, on the one hand, to inorganic compounds, on the other. The larger part of soil nitrogen exists, however, in complex organic combinations. Nevertheless, the simple inorganic nitrogen compounds,

[1] U. S. Dept. Agr., Bur. Soils Bul. 80 (1911).

especially nitrates, while occurring in relatively small amounts, have long been considered to be of great importance to plant growth.

For the purposes of this investigation two courses of procedure were open. First, a study of the changes that take place in the individual nitrogen compounds occurring in soils; second, a study of the group changes—that is, the effects of the treatment on the relative amounts and proportions of the large groups included under the amids, monamino acids, and diamino acids. The latter of these was chosen.

EFFECTS OF HEAT ON NITRATES.

The soils used in this investigation were taken from various localities in the islands and represent a wide range of types and conditions of formation. Some of the samples were taken from arid sections, some from intermediate, and still others from extremely humid sections. The method of heating differed somewhat from that employed in the work already reported. The time of heating was 2 hours, and the temperatures used were 100, 150, 200, 250° C. and steam heat in an autoclave at 2 atmospheres pressure. One hundred gram portions of air-dried soil placed in porcelain dishes were heated to the desired temperatures in an air bath, or autoclave. Nitrates were determined colorimetrically by use of the phenol disulphonic acid method, and ammonia, from separate portions, by distillation with magnesium oxid in the usual way. It should be remembered that the ammonia thus obtained probably occurred in part as amids. Distillation with magnesium oxid is known to liberate ammonia from amids. In a few instances the modified method of Schloesing,[1] which consists in leaching the soil with dilute hydrochloric acid and then distilling the ammonia from the filtrate with the use of magnesium oxid, was employed. The results were very similar to those obtained by direct distillation. The following table shows the effects of heat on the nitrate content:

The effects of heat on soil nitrates.

[Nitrate nitrogen expressed in parts per million of air-dried soil.]

Temperature.	Soil No. 9.	Soil No. 290.	Soil No. 292.	Soil No. 329.	Soil No. 335.	Soil No. 407.	Soil No. 411.	Soil No. 428.
Unheated	108.0	18.0	17.6	197.0	3.3	0.7	56.0	70.0
100° C.	95.0	18.6	13.0	158.0	2.0	.7	60.0	70.0
150° C.	57.0	12.5	23.5	61.5	3.0	.6	1.7	49.5
200° C.	5.0	6.5	3.5	1.3	.6	.5	1.5	.8
250° C.	5.4	.5	1.4	3.5	1.0	.4	.5	.5
Steam pressure 2 atmospheres	94.0	10.5	12.5	148.0	1.0	.6	48.0	46.0

These data are of interest as showing the destructive effect of heat on soil nitrates. In most instances the nitrates underwent considera-

[1] Referred to by Iodidi, Michigan Sta. Tech. Bul. 4, p. 11.

ble decomposition at 150° C., while at 200 and 250° C. practically total decomposition took place. Heating to 100° C. had but little effect. Steam heat at 2 atmospheres pressure brought about somewhat less decomposition than dry heat at 150° C.

EFFECTS OF HEAT ON THE AMMONIA CONTENT.

In the next table will be found the data showing the effects of heat on the ammonia content.

Effects of heat on the ammonia content of soils.

[Ammonia nitrogen expressed in parts per million of air-dried soil.]

Temperature.	Soil No. 9.	Soil No. 290.	Soil No. 292.	Soil No. 329.	Soil No. 335.	Soil No. 407.	Soil No. 411.	Soil No. 428.
Unheated	28.0	18.1	11.2	56.0	12.6	9.1	19.6	63.7
00° C	23.8	19.6	10.5	64.4	18.2	13.5	28.0	72.8
150° C	67.2	45.2	32.2	81.6	17.5	28.7	77.7	127.2
200° C	187.6	464.8	174.3	218.4	32.2	368.2	170.8	274.4
250° C	40.6	206.5	336.0	28.0	19.6	114.8	98.0	238.0
Steam pressure, 2 atmospheres	83.3	51.1	16.8	77.7	16.1	46.2	69.2	112.7

The ammonia content of soils Nos. 329 and 428 before heating is here shown to be abnormally high. Generally soils contain ammonia to the extent of a few parts per million only, whereas the nitrate content may rise to considerable concentration.[1]

Under the influence of heat the ammonia content of all the soils studied was greatly increased, practically reaching a maximum at about 200° C. Above this temperature a falling off took place which was probably due to a loss of ammonia through volatilization. We here have, therefore, some interesting and, as seems probable, very important facts. As pointed out above, heat considerably increases the solubility of the inorganic matter. Here it is shown that the ammonia content is enormously increased also.

Formerly little attention was given to the ammonia content of soils except in its relation to nitrification. During the past few years, however, the idea that ammonia may serve as a direct source of nitrogen to higher plants has steadily gained ground. It is now known that certain aquatic plants, rice in particular, not only can utilize ammonium nitrogen but that this form of nitrogen is better adapted to assimilation by rice[2] than is nitrate. Other crops[3] have also been found to be able to transform ammonia into proteids with

[1] Ammonia in soils, produced by biological agents, has for some time been looked upon as being merely a transitional state, its formation being essential to nitrification. The nitrifying organisms seize on the ammonia and convert it into nitrites and then into nitrates, thus effectively preventing an accumulation of ammonia in the soil at any one time. One of the essentials of vigorous nitrification, however, is free oxygen, while ammonification may take the place under anaerobic conditions. In many Hawaiian soils aeration is very low, and for this reason (perhaps others), nitrification frequently does not keep pace with ammonification.

[2] See Hawaiian Sta. Bul. 24.

[3] Krüger, Landw. Jahrb., 34 (1905), No. 5, p. 761.

equal facility. From the large number of cultures that have been reported and the many observations made it is safe to assume that the ammonia of natural soils is absorbed and assimilated to a greater or less extent by nearly all plants. We may conclude, therefore, that an important part of the action of heat on soils has to do with the production of ammonia.

As previously stated, Schreiner and Lathrop (page 29) have shown that the major portion of the organic nitrogen compounds, split off from more complex bodies in soils under the action of heat, is also beneficial to plant growth. With the additional production of relatively large amounts of ammonia it is probable that marked stimulation would result.

The effect of heat viewed from this standpoint is also of interest in its relation to the effects of partial sterilization. As already stated, one of the pronounced effects of partial sterilization, either with heat or volatile antiseptics, is the abnormal ammonification thus induced and which seems to be correlated with marked plant stimulation. In some Hawaiian soils the effect of partial sterilization on subsequent ammonification has recently been found to be exceptionally great. If the accumulation of ammonia as a result of partial sterilization reacts beneficially on plants, we certainly have a right to conclude that its direct production by means of heat would also prove stimulative to crops.

EFFECTS OF BRUSH BURNING IN THE FIELD.

With the view to determining the effects produced by burning refuse, brush, etc., in the field, a few samples of soil from spots where brush had been burned were examined at two different times. The brush was burned about September 1 and the samples were taken September 10 and November 7, respectively. Care was taken to remove the ashes so as to secure portions of the uncontaminated soil. Samples of unburned soil near by were taken at the same time. Ammonia and nitrates were determined in the samples as follows:

Effects of burning brush on soil nitrogen.

[Parts per million of nitrogen in air-dried soil.]

Laboratory No.	As nitrates.		As ammonia.	
	After 10 days.	Two months later.	After 10 days.	Two months later.
402 (burned)	6.5	5.5	50.4	100.8
402a (not burned)	20.0	18.0	39.2	70.0
403 (burned)	6.0	8.0	161.0	106.4
403a (not burned)	6.0	8.0	21.0	32.2
404 (burned)	16.0	22.0	77.0	114.8
404a (not burned)	52.0	52.0	8.4	30.8

Here again it is shown that an increase in the ammonia and a decrease in nitrates takes place in soil heating. The content of ammonia and nitrates at the end of two months is of special interest. The above data show that not only is ammonia formed by the action of heat but that subsequently ammonification took place at a greater rate in two cases out of three than in the unburned soils. Nitrification, however, was not restored under the existing field conditions. It is probable that reinoculation with both the ammonifying and nitrifying organisms gradually took place, but the lack of aeration prevented the development of the nitrifying bacteria. These soils had not been cultivated for two years previously and received no tillage during the time of observation. It is not possible to state the temperature to which the soil was heated in these instances. An approximate test applied in another locality, however, indicates that the burning of small brush heaps similar to those burned on the soils above discussed created a temperature of about 200° C. 6 inches below the surface. The temperature would naturally vary greatly from place to place.

EFFECTS OF HEAT ON THE ORGANIC NITROGEN.

Having found that large amounts of ammonia are formed from the action of heat, a study of the organic nitrogen as affected by heat seemed of interest. It is well known that ammonia is one of the cleavage products of protein hydrolysis. It is also known that in the destructive distillation of organic nitrogenous substances ammonia is one of the decomposition products. It was observed that the amounts of ammonia recovered from heated soils by means of distillation were not proportional to the total nitrogen present, but seemed to depend largely on the type of the soil. The amount of ammonia obtained, for example, from soil No. 335 was very much less than that from the other samples studied (page 32). Ammonia, therefore, was probably volatilized and driven out of the soil to a greater extent in some instances than in others. Soil 335 is a sandy soil composed very largely of coral sand ($CaCO_3$). In the foregoing work total nitrogen determinations were not made. Hence it is impossible to correlate the rise and fall of ammonia with losses of nitrogen.

In order to throw further light on these questions total nitrogen and the several groups of nitrogen compounds rendered soluble in boiling hydrochloric acid were studied. For this purpose the method of Hausmann[1] as modified by Osborne and Harris[2] was applied. This method was devised for a study of protein chemistry, but has been previously used by Jodidi and others in studying the organic nitrogen of soils.[3]

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[1] Ztschr. Physiol. Chem., 27 (1899), p. 95. [2] Jour. Amer. Chem. Soc., 25 (1903), p. 323.
[3] Michigan Sta. Tech. Bul., 4 (1909); Iowa Sta. Research Bul., 1 (1911).

In this study total nitrogen, nitrates, ammonia, amids, diamino acids, and monamino acids were determined. Nitrates and ammonia were determined in the soil directly, while the groups of organic compounds were determined in solutions obtained by boiling 50 grams of soil with 750 cubic centimeters of hydrochloric acid under a reflux condenser for 10 hours, as outlined by Jodidi, filtering, and making the filtrate up to 1 liter.

The organic nitrogen of soils, having at one time been bound up largely in proteid combinations, may reasonably be expected to yield hydrolytic products similar to those formed from protein. But little is known, however, regarding the specific hydrolysis induced by the microflora of the soil. It is not known, for example, whether the protein molecule as a whole is broken down with the ultimate liberation of ammonia from the several classes of protein cleavage products in the same ratio in which nitrogen occurs in them or whether certain of these groups yield inorganic or elementary nitrogen more readily than others.

Samples of both heated and unheated soil were studied in this connection. The former were subjected to a temperature of 200° C. for a period of two hours, after which the same treatment and determinations were made as in the unheated portions. The results are recorded in the following table:

Nitrogen compounds in heated and unheated soils.

Soil numbers.	Total nitrogen.	Nitrates.	Ammonia.	Soluble in hydrochloric acid.					Composition of hydrochloric acid soluble.			
				Amids.	Diamino acids.	Monamino acids.	Total.	Per cent of total.	Ammonia.	Amids.	Diamino acids.	Monamino acids.
Unheated:	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*		*P. ct.*	*P. ct.*	*P. ct.*	*P. ct.*
379	0.546	0.001	0.001	0.096	0.030	0.298	0.426	78.02	0.23	22.53	7.04	69.95
405	.179	.0001	.005	.042	.018	.100	.165	92.18	3.03	25.45	10.91	66.66
406	.504	.0015	.006	.079	.055	.240	.381	75.59	1.57	20.74	14.43	62.97
428	.779	.0045	.022	.129	.029	.363	.558	71.63	3.94	23.12	5.9	65.05
447	.396	.0062	.001	.074	.033	.125	.239	60.35	.41	30.69	13.80	52.30
Heated:												
379	.417	.0	.069	.098	.034	.168	.369	88.49	18.69	26.56	9.20	45.53
405	.178	.0	.036	.055	.017	.044	.152	85.39	23.68	36.18	11.18	28.95
406	.419	.0	.067	.103	.019	.092	.281	67.05	23.84	36.65	6.76	32.74
428	.608	.0	.031	.077	023	.079	.210	34.54	14.76	36.66	10.95	37.62
447	.207	.0	.020	.039	.022	.028	.109	52.65	18.35	35.78	20.18	25.69

Considering first the unheated soils, the nitrates and ammonia are shown to constitute a relatively small percentage of the total nitrogen and to vary greatly in the different soils examined. Soil 447 was found to contain the highest amount of nitrates, while in No. 405 nitrates were present to the extent of only one part per million. No. 428 contained an abnormally high ammonia content,

while Nos. 405 and 406 also contained many times as much ammonia as nitrates.

The relative amounts of nitrogen extracted by hydrochloric acid also varied greatly. In soil No. 405, 92.18 per cent of the total nitrogen went into solution, while No. 447 yielded only 60.35 per cent of its nitrogen. Nos. 405 and 406 are soils that have been devoted to aquatic agriculture (rice and taro) for many years, while soils 379, 428, and 447 have been subjected to dry-land cultures.

The chemical decompositions and hydrolyses that take place naturally in the organic matter of soils being brought about largely by biological agents, it is probable that the range and types of such reactions in submerged soils are somewhat different from those taking place in well-aerated soils. There are several lines of reasoning not necessary to mention here that lead to this conclusion. From this point of view, then, the biological effects on soil nitrogen may reasonably be expected to be different in the two instances. The nature of the organic matter originally incorporated with the soil probably has some bearing on this question also.

Among the several groups of nitrogen compounds brought into solution by hydrochloric acid it is noteworthy that the amids and monamino acids constitute the main portion. The latter comprises approximately two-thirds of the total nitrogen dissolved. It should be borne in mind, however, that the monamino nitrogen was determined by difference; that is, by subtracting the sum of the other groups from the total nitrogen in solution. It is known, however, that this difference is not made up entirely of monamino acids. Jodidi[1] found, for example, that the monamino nitrogen group in Iowa soils was made up of from 40.12 to 92.11 per cent of actual monamino acids, the variation in this respect being dependent in part on the treatment to which the soil had been previously subjected. It is of interest that the relative amounts of amids, monamino, and diamino nitrogen in Hawaiian soils were found similar to those of soils elsewhere.

Turning now to the question of heat as affecting soil nitrogen, it was found that with the exception of No. 405 the average loss of nitrogen was about 25 per cent, but in certain soils the loss was much greater than in others. Soil No. 447 suffered a loss of practically 50 per cent while No. 405 sustained almost no loss of nitrogen. It is also of interest that the reduction in the amounts of nitrogen extracted by hydrochloric acid was greater in two instances and less in three than the absolute loss of nitrogen occasioned by heat. In every instance enormous increases in ammonia and a total decomposition of nitrates took place. On the whole, the absolute amounts of neither the amids nor the diamino acids were greatly affected by

[1] Iowa Sta. Research Bul. 1 (1911).

heat, whereas there was relatively large reduction in the nitrogen of the monamino acid group in every soil studied.

Heating, therefore, caused a loss of nitrogen on the one hand and an increase in ammonia on the other, and the decompositions appear to come principally from the monamino acid group. The amounts of amids in soils Nos. 428 and 447 and the diamino acids in Nos. 406 and 447 also sustained considerable loss from the heating.

Regarding that portion of soil nitrogen remaining insoluble in hydrochloric acid, next to nothing is known. By again referring to the table (p. 35) it will be seen, however, that the heat had some effect on the insoluble nitrogen compounds. The difference between the total nitrogen in the soil and that extracted shows that considerable reduction in the insoluble nitrogen of soils Nos. 379 and 447 took place by heating, while there was a gain in the insoluble nitrogen of soil No. 428. The organic matter of soil No. 428 is in a less advanced stage of decomposition than that of the other soils studied and it was noticed that a pronounced charring in this soil took place under the action of the heat. It seems probable that such charring of the organic matter would tend to protect the nitrogen bodies in the interior of the particles from the action of the solvent, thus apparently increasing the percentage of insoluble nitrogen.

SUMMARY.

(1) Twelve different soils representing a wide range of types and agricultural conditions were studied with reference to the effects of heating to 100° C., to 250° C., and to ignition. The solubility of all the mineral constituents except sodium was determined, using water and fifth-normal nitric acid as solvents. The effects on the nitrogen compounds were also investigated.

(2) The results showed considerable variation. Neither the absolute nor the relative solubility of the inorganic constituents were effected similarly in all the samples studied.

(3) On the average, drying at 100° C. was found to bring about an increase in the water soluble manganese, lime, magnesia, phosphoric acid, sulphates, and bicarbonates. At this temperature an increase in the solubility of potash, silica, and alumina was produced in about 50 per cent of the soils examined, but a decrease was observed in the solubility of these elements in some instances. The solubility of iron was decreased in most instances.

(4) Heating to 250° C. or ignition produced effects on the solubility in water similar to those brought about at 100° C., but varying in degree, these being sometimes greater, sometimes less in intensity than those produced at 100° C.

(5) The solubility in fifth-normal nitric acid was not greatly affected by heating to 100° C., but in some instances heating to

250° C. considerably increased the solubility of alumina, manganese, potash, and phosphoric acid and at the same time effected a reduction in the solubility of lime and magnesia. Upon ignition the solubility of silica, alumina, potash, phosphoric acid, and sulphates was increased, while the solubility of lime and magnesia underwent a corresponding decrease.

(6) The solubility of soils used in aquatic agriculture is abnormally high, but upon drying out these become much less soluble and approach a state similar to that existing in aerated soils. When such soils are heated after drying they seem to undergo changes of the same order as are produced in dry-land soils.

(7) No single factor is sufficient to cover the solubility effects resulting from heating Hawaiian soil. On the other hand, the subject is very complex and involves many factors. Among the more important of these may be mentioned flocculation, deoxidation of manganese dioxid, oxidation, particularly of iron, double decomposition, dehydration, and the attending physical alterations of soil films. Such alteration would destroy film pressure, thus allowing the solvent to come into more intimate contact with the soil constituents. At the higher temperatures bicarbonates become converted into normal carbonates, thus effectively lowering the solubility of lime and magnesia.

(8) Nitrates undergo decomposition with heat, a decrease in nitrate content having been found to take place at 150° C., while at 200° or 250° C. practically total destruction of nitrates took place.

(9) One of the noteworthy effects of soil heating is the production of ammonia, which at 200° C. was formed in abnormally large amounts. Soil subjected to heat from brush burned in the field was found to undergo stimulated ammonification after heating. Nitrification, on the other hand, was not restored after the lapse of two months.

(10) Heating to 200° C. caused a loss of approximately 25 per cent of the total nitrogen. A loss of nitrogen and the ammonia formed by the action of heat came largely from the monamino acid group, while the amids and diamino acid sustained much less loss.

(11) The results of these studies are believed to throw important light on the subject of soil aeration and consequently have a direct bearing on the practical question of soil management.

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